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A Method for Marking Paper and Cardboard

10 The present invention relates to a method for generating a permanent mark in the top coating of paper substrates, and to paper products, such as paper and cardboard, having a mark in the top coating which are obtainable by such method.

15 There is often a need to provide paper substrates of various basis weights permanently with a name, image, design, logotype or some other marking, especially a safety marking. For this purpose, watermarks have proven useful in the past. So-called true watermarks, which are based on local thickness variations of the paper stock, can be generated by conventional methods, extensively described in the prior art, by pulp lessening on the wire of the papermachine. Alternatively, as described in
20 DE-A-34 31 577, local variations of the thickness of the paper can be produced on the papermaking wire using a pulsed mass jet, such as water or air, or a laser impulse. In the finished paper, the lessened areas appear as brighter areas in transmission. Another possibility for the marking of paper substrates
25 is embossing, as described in WO-A-97/17493.

DE-A-34 25 086 describes a method for marking prints by exposing the printed sheet/the printed web to a special form of energy. As the form of energy, modulated laser light, visible light, infrared light, ultraviolet light or ultrasound are
30 proposed. As a result of such energy treatment, part of the printing is ablated in predetermined areas which yields the marking on the print. The method is especially suitable for producing unique specimens (unica) of a print.

DE-A-37 10 153 describes a paper provided with an image and coated with microcapsules, e.g., autocopying paper. In the method for producing this paper, the paper substrate is first provided with an image in terms of a watermark using laser energy. Then, a transparent microcapsule coating is applied to the surface of the paper substrate, covering, but not obscuring the image produced by laser energy. Thus, the image remains visible through the dry microcapsule coating of the finished product. The image should not interfere with subsequent processes, especially printing or writing on the paper.

It has been the object of the present invention to provide a method enabling the generation of a permanent marking in an opaque top coating, e.g., printing, metal coating or paint coating, on paper substrates of various commonly used basis weights without the need to subject the paper substrate which is already provided with such top coating to another process step for marking.

This object has been achieved by a method for generating a mark in the top coating of paper substrates by treating the surface of at least one layer positioned below the top coating with laser energy prior to application of the top coating, wherein the top coating of the paper substrate is opaque and selected from at least one printing and/or at least one paint coating and/or at least one metal coating, or combinations thereof.

The fibrous web substrates which may be employed as the paper substrate in the method according to the invention, which may optionally be coated prior to the laser treatment, have a basis weight of from 40 to 400 g/m², preferably from 60 to 300 g/m². Therefore, cardboard is also suitable for the method according to the invention; it usually has a basis weight of at least 150 g/m², preferably at least 170 g/m². Thus, the terms "paper substrate" or "substrate of the paper product" which are used interchangeably to describe the invention not only comprise

substrates of classic papers, such as writing paper, but also substrates having a basis weight corresponding to that of cardboard.

5 The opacity of the top coating is determined by subtracting the opacity (in percent) of an uncoated paper substrate from the opacity (in percent) of the same paper substrate when it has been coated. The determination of the opacities of the individual coated and uncoated paper substrates is performed according to DIN 53146. The areas compared are those not treated with
10 laser energy. Such printing and/or paint coating and/or metal coating is considered opaque within the meaning of the invention if it causes an increase in opacity of at least 5 absolute percent, preferably at least 8 absolute percent, on a conventional office paper having a basis weight of 80 g/m^2 . As the
15 standard paper substrate for determining the opacity of the top coating(s), common writing paper treated with an unpigmented starch coating having an opacity (uncoated) of 80-82% was used.

In the context of the present invention, the terms "opaque" and "non-transparent" in describing the top coating are used interchangeably.
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Rather surprisingly, it has been found that the marking generated by the action of laser energy (laser beam) on the surface of a layer of the paper substrate positioned below the non-transparent top coating is continued on the overlying printing(s) and/or paint coating(s) and/or metal coating(s) and can
25 be seen or discerned on the surface of such top coating in reflection without difficulty as a change in color density, color position, gloss and/or reflection. This effect is important, in particular, for paper substrates of higher basis weights, such as cardboards having at least 150 g/m^2 , which are
30 as such not transparent at all, i.e., a classic watermark would be of no use anyway.

The technical effect caused by the method according to the invention is surprising, in particular, because the top coating positioned over the layer marked with the laser according to the invention is a non-transparent, i.e., opaque, coating.

5 According to the invention, this top coating consists of at least one printing and/or at least one metal coating and/or at least one paint coating, or combinations of such coatings, which may also be present in various orders.

10 Thus, several successive coatings forming the top coating may follow the laser-marked surface of the paper substrate without adversely affecting the discernability/visibility of the mark on the top coating in reflection. Therefore, according to the invention, it is also possible to apply several printings, metal coatings or paint coatings or combinations of those
15 different layers over one another. Thus, for example, printing with at least three colors and black as a contrast enhancer is necessary for color printing. Immediately below the top coating consisting of said printing and/or paint coating and/or metal coating, there may be an unpigmented, white or color pigmented
20 coating which may additionally be densified (supercalendered).

Thus, according to the invention, the top coating positioned over the laser-marked surface, which as such is non-transparent, may consist of several different individual coatings, such as a metal coating and an overlying paint coating and/or
25 printing, or an unpigmented, white or color pigmented coating which may additionally bear a printing or paint coating.

The printing is effected, in particular, with offset, intaglio and flexographic printing methods, ink jet printing, laser printing, as known from the prior art.

30 The metal coating of paper substrates can be effected by the methods known in the prior art, for example, by direct or transfer processes. Aluminum, copper, gold and silver are

especially suitable for being applied to paper substrates as the metal layer. In a particular embodiment, the top coating consists of a metal coating which is selected from the metals mentioned. This metal coating may additionally be printed
5 and/or painted.

Metal coatings with one of the above mentioned metals, useful according to the invention, have an average layer thickness of from 10 to 50 nm, preferably from 15 to 30 nm, more preferably from 15 to 25 nm. Metal coatings having a layer thickness of as
10 low as 10 nm on paper with a basis weight of 80 g/m² and an opacity of 80-82% result in an increase in opacity of over 8 absolute percent as compared with non-metallized paper.

The painting of paper substrates is also known in the prior art. Due to its comprising corresponding pigments and/or dyes,
15 the paint coating is white or colored.

When the method according to the invention is performed, a paper or cardboard substrate, i.e., a fibrous web, a surface-treated fibrous web, a coated fibrous web which may optionally be treated and/or metal-coated below its coating, or a metal-coated fibrous web which may optionally be treated and/or
20 coated below its metal coating, is treated with laser energy at its surface. The method according to the invention may as well be performed in such a way that the laser energy is made to act on the fibrous web while still wet during the preparation of the web. The fibrous web may be a natural fibrous web. The
25 fibrous web itself may be transparent or opaque, white or colored, and may be surface-treated, for example, with an unpigmented or pigmented starch solution.

The optionally surface-treated fibrous web may additionally be
30 coated with an unpigmented, white or color pigmented coating which may additionally be densified (supercalendered) and optionally be coated with a paint.

One particular embodiment of the method according to the invention is characterized in that the surface of a fibrous web is treated with laser energy, and at least one further coating which is selected from printing, paint coating and metal coating is applied to the surface which has been treated with laser energy.

A further particular embodiment is characterized in that the surface of the fibrous web is treated with laser energy, the surface treated with laser energy is metal-coated, and then a printing and/or paint coating is applied to the metal-coated surface. As to the metal coating, the layer thickness of the metal coating and its preparation, reference is made to the above statements. Aluminum is the preferred metal coating.

Another particular embodiment is characterized in that the metal-coated surface of a fibrous web, optionally after applying a paint coating or printing, is treated with laser energy, and then a printing and/or paint coating is applied to the surface which has been treated with laser energy. As to the metals, layer thicknesses and preparation methods useful for said metal coating, reference is made to the above statements.

Another particular embodiment is characterized in that the surface of a fibrous web which is provided with an unpigmented, white or color pigmented coating is treated with laser energy, and then a printing and/or paint coating is applied to the surface which has been treated with laser energy. Said unpigmented or pigmented coating may additionally be densified (supercalendered) and optionally be coated with a paint.

Another particular embodiment of the method according to the invention is characterized in that the surface of a fibrous web which is provided with the above described unpigmented or pigmented coating is treated with laser energy, the surface treated with laser energy is metal-coated, and then a printing

and/or paint coating is applied to the metal-coated surface. As to the metals, layer thicknesses and preparation methods useful for said metal coating, reference is made to the above statements.

5 Another embodiment is characterized in that the surface of a fibrous web which is provided with the above described unpigmented or pigmented coating is metal-coated, the metal-coated surface, which may optionally be provided with a paint coating or printing, is treated with laser energy, and then a printing
10 and/or paint coating is applied to the surface which has been treated with laser energy. As to the metals, layer thicknesses and preparation methods useful for said metal coating, reference is made to the above statements.

15 Another embodiment according to the invention is characterized in that the surface of a fibrous web is treated with laser energy, the surface treated with laser energy is provided with the above defined unpigmented or pigmented coating, and then a printing and/or paint coating is applied.

20 The mark which can be seen in the top coating, i.e., the printing, paint coating or metal coating, is usually a logotype, a name, a trade mark, an image, a design, a safety marking or another marking which facilitates the identification of the printed or written-on paper.

25 As to the laser treatment of surfaces of paper, reference may be made to the prior art, for example, the disclosure of DE-A-37 10 153 and the references cited therein.

30 According to the invention, the laser treatment for writing on or marking the substrate can be effected with the known raster-scanning method, or by vector scanning with x-y galvanometer mirrors, polygon scanners or mask imaging methods.

The laser energy required for performing the method according to the invention may be supplied by a pulsed laser or a continuous-wave laser, typically a carbon dioxide laser in either case. In the practice of the invention, Nd:YAG lasers, frequency-converted Nd:YAG lasers, copper vapor lasers, excimer lasers and diode lasers may also be used. The laser energy is in each case applied to the layer immediately beneath the top coating, prior to applying the top coating.

Usually, the energy density of the laser has to be set in such a way that the image generated on the surface of the laser-treated layer is visible or at least discernible. Those skilled in the art know that this not only depends on the kind of laser (pulsed or continuous-wave laser) and its energy level, but also on the type of paper and its water content. To generate visible or discernible images on paper with low to normal moisture contents (3 to 8% by weight), DE-A-37 10 153 recommends energy densities within a range of from 1.7 to 5.0 $\text{Joule}\cdot\text{cm}^{-2}$ for pulsed lasers and from 2.2 to 4.8 $\text{Joule}\cdot\text{cm}^{-2}$ for continuous-wave lasers, depending on the web speed. For papers having a higher moisture content, correspondingly higher laser energies are required. When continuous-wave lasers are used, distance-related energies (quotient of laser power/laser scanning speed) of from 3 to 12 J/m, preferably from 5.5 to 8 J/m, are preferred for papers with low to normal moisture contents. For papers with high moisture contents, which may be up to 90% by weight, distance-related energies of up to 150 J/m are required.

In the method according to the invention, it is also possible to select the energy density of the laser in such a way as to generate no visible or discernible images on the substrate treated therewith. In this case, the energy density may be between 0.1 and less than 1.7 $\text{Joule}\cdot\text{cm}^{-2}$, preferably between 0.1 and 1.6 $\text{Joule}\cdot\text{cm}^{-2}$, more preferably between 1.0 and 1.6 $\text{Joule}\cdot\text{cm}^{-2}$. The changes at the surface of the paper or the

coating of the paper caused by such energy densities are not visible or discernible in transmission or reflection, but result in the generation or visualization of a mark only in the subsequent coating or coatings. Thus, the method according to the invention may typically be performed with laser energy densities of from 0.1 to 5.0 Joule·cm⁻², wherein only the surface to be coated is modified by exposure to a laser, as described above. This modification is not necessarily immediately visible/discernible, but may result in the recognizable changes described hereinbelow only in the top coating applied thereon.

The method according to the invention may independently be performed on one or both sides of the paper or cardboard substrate.

By the method according to the invention, i.e., by the treatment of the coated or uncoated paper substrate with laser energy, a surface is generated which behaves differently in a subsequent further coating process, especially a metal coating or printing process, as compared to a material which has not been laser-treated. This change in the surface is continued in the subsequent coating (printing, paint coating, metal coating) and results in easily recognized changes in color density, color position, gloss and/or reflection therein.

In the case where the laser energy is adjusted so as to generate no visible or discernible image in the substrate treated therewith, as described above, and if the coating applied thereon is not opaque according to the above definition, but transparent, the mark may nevertheless be discernible in such coating through a change in reflection and mattness of the surface of the transparent coating.

Possible transparent coatings which are applied to the laser-marked layer are selected from those in which the increase in

opacity as determined according to the above described method is 2.5 absolute percent or less, preferably 2 absolute percent or less.

Transparent coatings for paper substrates are known in the prior art, and they are distinguished from each other on the basis of whether the component constituting the transparent coating is dispersed or dissolved in a suitable medium (aqueous or organic solvent) for application. Examples of transparent coatings or paints are those comprising nitrocellulose (nitrocellulose lacquers) or acrylates (acrylic paints).

It is also possible to treat not only one, but the surface of several layers provided on the fibrous web with laser energy prior to applying the top coating, which results in a mark on the top coating which as such has different color densities, color positions, glosses and/or reflections. However, it is preferred to treat the surface of only one layer with laser energy.

Various types and degrees of reflection can be produced on the subsequent coating or coatings by selecting the mode of laser marking, i.e., by appropriately adjusting the laser energy, focus geometry, spot size, line spacing and line orientation.

With the method according to the invention, it is possible to transfer digitalized image patterns to the paper which is not yet finally coated, especially printed, metal coated and/or paint coated. The image then becomes visible in the top coating after the final coating step, i.e., after the printing, paint coating or metal coating. Thus, the method according to the invention allows to visualize the mark only in the top coating whereas conventional "watermark" methods aim at visualizing the mark within the paper substrate itself. For fibrous web substrates of higher basis weights, such as cardboards with at

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The invention is further illustrated by the following non-limiting Examples.

Examples:

Reference Examples

- 5 The influence of different top coatings on the increase in opacity of paper substrates was determined. Thus, the opacity of the paper substrate without a coating was subtracted from the opacity of the paper substrate provided with the top coating in order to obtain information about the opacity or covering power of the coating itself. The difference was converted into a percentage which corresponds to the absolute increase in opacity in absolute percent brought about by the coating. The opacity of the paper before and after coating was in each case determined according to DIN 53146.

Table 1

- paper substrate - basis weight	top coating	increase in opacity in absolute percent as compared to the uncoated paper substrate	remarks
- autocopying raw paper - 55 g/m ²	- microcapsule coating - 5 g/m ² dry coating weight	1.3-2.5	<u>1</u>
- ZETA® office paper - 80 g/m ²	- microcapsule coating - 5 g/m ² dry coating weight	0.8-2.0	<u>2</u>
- ZETA® office paper - 80 g/m ²	- ink jet printing	9.0-12.4	<u>3</u>
- ZETA® office paper - 80 g/m ²	- offset printing	8.0-12.3	<u>4</u>
- ZETA® office paper - 80 g/m ²	- aluminum coating - about 10 nm layer thickness	≥ 8.5	<u>5</u>

Remarks for Table 1:

1: Example according to EP 0 240 259

2: ZETA[®] = registered trademark of the Zanders Feinpapiere AG, Germany, common writing paper treated with an unpigmented starch coating, having an opacity of 80-82% (uncoated)

3: Hewlett Packard DeskJet 870 ink jet printer, measured for the Hewlett Packard ink jet colors red, green and blue, normal printing mode

4: laboratory proofing machine (Prüfbau), offset colors red and blue, medium color density

5: metal coating according to EP 0 098 368

The printing, paint coatings or metal coatings in the following Examples respectively caused increases in opacity of at least 8 absolute percent on the above mentioned ZETA[®] office paper. The ink jet and offset printing and the metal coating was respectively performed as described in the Reference Examples.

Example 1

In this Example, a continuous-wave carbon dioxide laser with a power of 30 Watt was used to provide a fibrous web on a paper-machine wire having a water content of 88% by weight with marks of 6 x 35 mm using a distance-related energy (quotient of laser power/laser scanning speed) of 120 J/m. The fibrous web was dried to a moisture content of 6-7% by weight and had a basis weight of 85 g/m².

After drying, the paper was printed with offset and ink jet printing methods.

In both printing methods, the laser marks are visible in reflection and of good quality.

Example 2

In this Example, a carbon dioxide laser system pulsed with 100 Hz (nominal value) with a pulse energy of 3.27 J to 5.27 J was used to provide a fibrous web on a papermachine wire having a water content of 88% by weight with marks of 0.64 cm² using shadow projection. The fibrous web was dried to a moisture content of 6-7% by weight and had a basis weight of 85 g/m².

After drying, the paper was printed with offset and ink jet printing methods.

It was found that an energy density of 8.0 J/cm² was a minimum threshold for the generation of visible marks in both printing methods.

Example 3

In this Example, a continuous-wave carbon dioxide laser with an output power of 30 Watt was used to provide white and colored "natural papers" with a basis weight of 80 g/m² coated with an unpigmented starch solution and having a moisture content of about 6-7% by weight with marks of 13 x 70 mm using an operating power of 3 Watt and a distance-related energy of 6 J/m.

After applying the marks, the surfaces provided with a mark were printed with offset and ink jet printing methods.

In both printing methods, the laser marks are visible in reflection and of good quality.

Example 4

In this Example, a base paper with a basis weight of 200 g/m^2 was coated on one side with an aqueous pigmented paint formulation using cast coating methods to give dry coating weights of
5 nearly 20 g/m^2 , and finished in a high-gloss drying plant.

Subsequently, a continuous-wave carbon dioxide laser with an output power of 30 Watt was used with a testing device to generate marks of $13 \times 70 \text{ mm}$ in the coating of the thus produced paper using an operating power of 3 Watt and a distance-
10 related energy of 6 J/m .

After applying the marks, the surface provided with a mark was printed with offset printing methods.

After printing, the marks were visible in reflection and of good quality.

15 Example 5

In this Example, a continuous-wave carbon dioxide laser with an output power of 30 Watt was used to generate marks of $13 \times 70 \text{ mm}$ on various white, coated or uncoated, papers using a distance-related energy of 6 J/m , whereafter the papers were
20 metal-coated by metal vapor deposition methods on the surfaces marked with laser radiation.

The basis weights of the papers used were 55, 80 and 220 g/m^2 for the uncoated papers, 70 and 250 g/m^2 for the papers coated on one side, and 90 and 200 g/m^2 for the papers coated on both
25 sides, and the moisture content ranged from 6 to 8% by weight.

It was found that, independently of the type of paper (uncoated/coated) and its basis weight, the marks obtained after metal coating were brighter/darker in reflection depending on

the kind of illumination, and thus provided a contrast to the surface of the paper not provided with a mark.

The metal-coated paper was tested^o for functional usefulness using the paper as a printing medium, and its usefulness proved
5 satisfactory.

Example 6

This Example shows how the marks formed by laser irradiation vary with different energy levels.

10 The papers employed are the same as those employed in Example 5, and the distance-related energy of the laser radiation was varied from 3 to 12 J/m.

15 It was found that a distance-related energy of below 5 J/m is an approximate minimum threshold for uncoated papers, and 4 J/m for coated papers, for a mark to be visible after metal coating.

20 Visible marks are always obtained with distance-related energies of 5.5 to 8 J/m. Distance-related energies of > 8 J/m yielded marks with good visibility after the metal coating, but the papers already showed relatively severe carbonization phenomena in the region of the marks prior to metal coating.

Example 7

25 In this Example, a continuous-wave carbon dioxide 1 kW laser was employed with shadow projection through a mask to generate marks on different papers (uncoated/coated; white/colored) at different web speeds and on a testing device, as shown in the following Table 2:

Table 2

type of paper basis weight (g/m ²)	color of paper	web speed (m/min)
55 uncoated	white	175
80 uncoated	white	175
80 uncoated	light blue	200
220 uncoated	white	200
70 coated on one side	white	200
250 coated on one side	white	200
250 coated on one side	blue	200
90 coated on both sides	white	200
200 coated on both sides	white	200

The size of the mark was 11 x 12 mm in each case. After applying the marks, the surfaces provided with a mark were metal-coated using metal vapor deposition. The marks obtained after the metal coating had good visibility in reflection and of acceptable quality. The metal-coated papers were tested according to Example 5 and proved satisfactory.

Example 8

- 10 In this Example, a carbon dioxide laser system pulsed with 100 Hz (nominal value) with a pulse energy of 2.0 J was used to provide a white uncoated 55 g/m² paper and a white 70 g/m² paper coated on one side with marks using shadow projection at web speeds of from 50 to 350 m/min.
- 15 At a size of the mark of 10 x 8 mm, corresponding to an energy density of 2.5 Joule/cm², and for different repetition rates, the marks showed good visibility in reflection.

After applying the marks, the surfaces provided with a mark were metal-coated using metal vapor deposition. The marks ob-

tained after the metal coating were visible in reflection and of acceptable quality. The metal-coated papers were tested according to Example 5 and proved satisfactory.

Example 9

5 In this Example, a continuous-wave carbon dioxide laser with an output power of 30 Watt was used to provide 55 g/m² base papers having a moisture content of 6-7% by weight with marks of 13 x 70 mm using an operating power of 3 Watt and a distance-related energy of 6 J/m, whereafter the base papers were coated
10 on one side, both on the marked and on the unmarked surfaces, with an aqueous, microcapsule-free, pigmented painting formulation as is used for cast coated papers, with dry coating weights of approximately 20 g/m².

The papers finished in a high-gloss drying plant showed marks
15 with acceptable visibility in each case; they were tested for functional usefulness, and their usefulness proved satisfactory.

Example 10

This Example shows how the marks formed by laser irradiation
20 vary with different energy levels.

The base paper and the laser were as described in Example 9, and the distance-related energy of the laser radiation was varied from 5 to 12 J/m.

25 It was found that a distance-related energy of below 5 J/m is a minimum threshold for a visible mark to be formed. Visible marks were always obtained with distance-related energies of 5.5 to 9 J/m. Distance-related energies of > 9 J/m yielded marks with good visibility, but the base papers already showed

relatively strong carbonization phenomena in the region of the marks.

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